Advanced Supported Liquid Membranes for CO_2 Control in Extravehicular Activity Applications

David T. Wickham,[1] Kevin J. Gleason,[2] and Jeffrey R. Engel[3]
Reaction Systems, LLC, Golden, Colorado, 80401

Scott W. Cowley[4]
Colorado School of Mines, Golden, Colorado, 80401

and

Cinda Chullen[5]
NASA Johnson Space Center, Houston, Texas, 77058

Developing a new, robust, portable life support system (PLSS) is currently a high priority for NASA in order to support longer and safer extravehicular activity (EVA) missions. One of the critical PLSS functions is maintaining the carbon dioxide (CO_2) concentration in the suit at acceptable levels. Although the Metal Oxide (MetOx) canister has worked well, it has a finite CO_2 adsorption capacity. Consequently, the unit would have to be larger and heavier to extend EVA times. Therefore, new CO_2 control technologies must be developed to meet mission objectives without increasing the size of the PLSS. Although recent work has centered on sorbents that can be regenerated during the EVA, this strategy increases the system complexity and power consumption. A simpler approach is to use a membrane that selectively vents CO_2 to space. A membrane has many advantages over current technology: it is a continuous system with no theoretical capacity limit, it requires no consumables, and it requires no hardware for switching beds between absorption and regeneration. Unfortunately, conventional gas separation membranes do not have adequate selectivity for use in the PLSS. However, the required performance could be obtained with a supported liquid membrane (SLM), which consists of a micro porous material filled with a liquid that selectively reacts with CO_2 over oxygen (O_2). In a current Phase II SBIR project, Reaction Systems has developed a new reactive liquid, which has effectively zero vapor pressure making it an ideal candidate for use in an SLM. The SLM function has been demonstrated with representative pressures of CO_2, O_2, and water (H_2O). In addition to being effective for CO_2 control, the SLM also vents moisture to space. Therefore, this project has demonstrated the feasibility of using an SLM to control CO_2 in an EVA application.

Nomenclature

°C	=	degrees Celsius
AP-Mim	=	1-(3-aminopropyl)-3-methylimidazolium
atm	=	atmospheres

[1] President and Principal Investigator, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.
[2] Senior Engineer, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.
[3] Senior Engineer, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.
[4] Professor of Chemistry, Department of Chemistry and Geochemistry, Golden, CO, 80401.
[5] Project Engineer, Space Suit and Crew Survival Systems Branch, Crew and Thermal Systems Division, 2101 NASA Parkway/EC5

B-DMAPyr = 1-butyl-4-(N,N-dimethylamino) pyridinium
Btu/h = *British thermal units per hour*
cm^2 = square centimeters
cm-Hg = centimeters of mercury
CO_2 = carbon dioxide
dp = *change in pressure*
dt = *change in time*
EVA = extravehicular activity
g = gram
g/h = grams per hour
IL = ionic liquid
ISS = *International Space Station*
K = Kelvin
kcal/h = kilocalorie per hour
kDa = kilodalton
kg = kilogram
MHz = megahertz
m^2 = square meters
mm Hg = millimeters of mercury
mtorr = millitorr
N_2 = nitrogen
NMR = nuclear magnetic resonance
O_2 = oxygen
P = pressure
P_O = initial pressure
Pm = Permeability
PLSS = portable life support system
RC = regenerated cellulose
RCA = rapid cycle amine
s = second
S = solubility
scc = standard cubic centimeters
SLM = supported liquid membrane
t = time
wt% = weight percent
μm = micrometers

I. Introduction

New, robust, lightweight life support systems are critical enabling technologies required for human exploration beyond low earth orbit (LEO). Moreover, the successful development of new systems would help preserve America's role as the world leader in space exploration for the foreseeable future as it carries out more and more difficult missions, including flights to near-Earth asteroids (NEAs), the Moon, and eventually MarsAs these missions develop, it is anticipated that crew members will spend extended time outside of space craft and established habitats, and therefore the agency is focused on the development of new, robust, lightweight life support systems for EVA. One area critical to life support is the control of CO_2 and new space suits must be able to accommodate longer EVAs without increasing the size or weight of the PLSS. Since the lifetime of the sorbent currently used for CO_2 control can be a limiting factor in EVA duration, the development of lighter, simpler, and reliable methods for CO_2 control is a primary need to support advanced exploration. [1,2]

The rate of CO_2 generation varies with the metabolic rate of the crew member. Recent studies of CO_2 control technology have been carried out in which the CO_2 injection rates were varied to match simulated metabolic rates. The average CO_2 generation rate was determined to be 0.093 g/h per Btu/h of metabolic rate of activity. [3] Assuming that the metabolic rate over an EVA is approximately 1000 Btu/h, then the average rate of CO_2 production is 93 g/h. In addition, based on recent findings regarding the effect that CO_2 has on decision making capability, NASA also

has a current interest in reducing the maximum allowable CO_2 concentration in the suit from 7.6 mm Hg to 2.8 mm Hg. [4] Thus, in order to carry out EVA operations safely, the CO_2 control system must be sized to handle at least average production rates for the duration of the EVA, which likely will last in excess of eight hours.

A. Current Methods for Carbon Dioxide Control for Extravehicular Activity and on Spacecraft

Currently, a sorbent is being used for CO_2 control during EVA, specifically, the MetOx system. The MetOx employs a metal oxide sorbent, which reacts with CO_2 at low temperature to produce the metal carbonate. During an EVA operation, the metal oxide is gradually converted to the metal carbonate and once all of the oxide has been converted, the canister is no longer effective. After the EVA, the canister is placed in a specially designed oven on-board the spacecraft, heated in a flow of air to about 200°C causing the carbonate to decompose back into the oxide, regenerating the activity of the MetOx for the next mission. Since the MetOx canister cannot be regenerated during the EVA, its capacity can be a limiting factor in the mission duration. The only way to increase EVA time is to increase the size and weight of the canister. Thus, new methods are needed to control metabolic CO_2 production. The new system must be robust, lightweight, and reliable. Several approaches to address this challenge are summarized below.

The technology being developed to replace the Metox is the Rapid Cycle Amine or RCA. [5,6,7] This unit cycles two vacuum-regenerable sorbent beds, rapidly alternating between CO_2 adsorption and off-line regeneration by exposure to space vacuum. The most recent results show that it can control CO_2 down to levels of 2.65 mm Hg and moisture to 15% relative humidity. The primary advantage of this approach is that there is no finite limit on capacity and therefore the size of the system does not have to scale with mission time.

However, there are some inherent disadvantages associated with a regenerable system. First, the hardware needed to carry out bed regeneration during EVA increases power requirements along with the size and weight of the system. In addition, the valve that cycles the beds between absorption and regeneration is a vulnerability because it must cycle frequently and its failure would mean an immediate failure of the entire RCA. Finally, each time a bed is regenerated, the O_2 contained in the volume is lost to space. Moreover when the astronaut is working at high metabolic rates, the beds have to be cycled more rapidly and therefore the O_2 losses scale with CO_2 production rate. For example, at the a metabolic rate about two times average, the O_2 losses were about 5 g/h and higher metabolic rates would result in higher O_2 losses.

B. Use of Membranes for CO_2 Control

The simplest way to control CO_2 is to use a membrane that allows CO_2 to escape to space vacuum while retaining O_2. A membrane system has several significant advantages over the other methods of CO_2 control. It would be a continuous system with no limit on the amount of CO_2 that is contained in a mission, it would be very simple and not require any moving parts, it would have low power demand, and it will be very reliable. Finally, with a membrane, the O_2 losses are independent of metabolic output. However, the CO_2 flux through the membrane scales with CO_2 concentration, which will help prevent crew exposure to high CO_2 concentrations during periods of increased CO_2 generation.

However, successful application of a membrane requires that some difficult challenges be met. First, the permeation rate of CO_2 through the membrane must be high enough that a reasonably sized membrane module can control an average metabolic CO_2 generation rate. In addition, the membrane must have good selectivity for CO_2 over O_2 in order to prevent unacceptably high O_2 losses. Each of these is discussed in more detail in the following section.

A. Estimates of Membrane Performance Requirements

Estimates of required CO_2 permeance are based on the volume limit of 0.25 ft^3, which is the size of the rapid cycle amine.[8] Seader and Henley[9] indicate that hollow fiber modules, can produce surface area to volume ratios from 500 to 9000 m^2/m^3. Using an intermediate value of 7000 m^2/m^3 (or 198 m^2/ft^3), we conclude that a module that has a volume of 0.25 ft^3 could contain a total surface area of 49.6 m^2 (496,000 cm^2). The module needs to control at least the average CO_2 production rate of 93 g/h (or 14.4 scc CO_2/s) and therefore the required CO_2 flux through the membrane is 3.12E-5 scc/(cm^2 s). Finally, with a maximum allowable CO_2 partial pressure of 0.30 cm Hg (3.0 mm Hg) in the suit, the flux and be converted to a permeance of 1.04E-5 scc/(cm^2 s cm Hg).

Finally, the membrane must have a low enough O_2 permeance to prevent excessive O_2 losses. Although achieveing a zero O_2 loss rate is desirable, a more reasonable first approximation is to set the maximum acceptable O_2 loss rate at the same value that is lost through leakage in the suit. Watts et al [10] indicate that suit leakage rates can reach 4.2 g/h (0.90 scc/s) and this rate is also within the range of O_2 losses reported for the RCA. Therefore, setting the maximum loss rate in a SLM at 4.2 g/h is a reasonable starting point. With a membrane area of 496,000 cm^2 and an exposure pressure of 22.8 cm Hg (0.3 atm), an O_2 loss rate of 4.2 g/h would be produced with an O_2 permeance of 7.89E-8 (scc/cm^2s cm Hg). Thus the CO_2/O_2 selectivity is [1.04E-5 scc/(cm^2 s cm Hg)/7.89E-8 scc/(cm^2 s cm Hg)] or 1300.

Unfortunately, conventional polymeric gas separation membranes, which rely on the physical differences between gas molecules have not been able to meet the requirements outlined above because of the inherent trade-off between selectivity and permeability. [3] For example, poly(dimethyl)siloxane has adequate CO_2 permeability but has a CO_2/O_2 selectivity of only about five.

B. Supported Liquid Membrane

Another approach is to take advantage of the difference in chemical properties of CO_2 and O_2 by incorporating an immobilized, reacting compound into the membrane as a supported (or immobilized) liquid membrane (SLM). In this application, the immobilized liquid would form a metastable complex with CO_2 on the crew side of the membrane. Because CO_2 is an acidic compound, a basic liquid could be an effective reagent. The complex would then diffuse through the liquid contained in the membrane pores, ultimately reaching the vacuum side of the membrane where the absence of gas phase CO_2 would shift the equilibrium, thereby resulting in the decomposition of the metastable complex, the release of the CO_2, and the regeneration of the sorbent. This process is frequently referred to as facilitated transport. SLMs effectively combine the absorption and stripping processes into one unit operation (Figure 1). On the other hand, because O_2 does not have acidic properties, it should not react with the liquid, resulting in potentially high CO_2/O_2 selectivity.

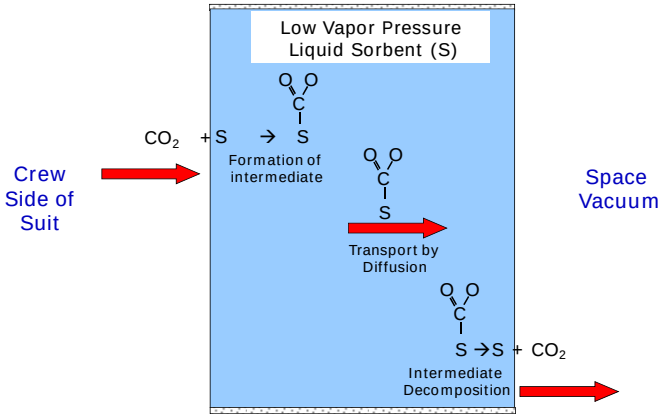

Figure 1. Schematic of facilitated CO_2 transport within a membrane pore.

In order to have adequate performance, the liquid reagent material must meet several criteria. First, because the membrane operates at constant temperature, the liquid must be fully regenerable by exposure to space vacuum and not require any temperature change to increase capacity. Second, the liquid must have low viscosity so the complex can diffuse quickly from one side of the membrane to the other. Third, and perhaps most important, the liquid reactant must have effectively zero vapor pressure so it is not lost by evaporation to space.

Amines have been shown to have excellent reversible CO_2 absorption capacity. They are commonly used to absorb CO_2 out of industrial gas streams and, are currently being evaluated in a cycling bed configuration to control CO_2 in EVA. The affinity of an amine for CO_2 depends on its structure. Primary amines (left side of Figure 2) bind CO_2 very strongly, usually requiring that the sorbent be heated for regeneration. On the other hand, secondary and tertiary amines (center and right side of Figure 2) do not bind CO_2 as strongly and therefore some can be regenerated by simply reducing pressure, a requirement for use in a membrane. Unfortunately, the vapor pressures of conventional amines are too high to be exposed to space vacuum and therefore they must be modified to prevent loss. In the RCA system, the amines are anchored to an ion exchange bead; however, this approach would not suitable for use in a membrane.

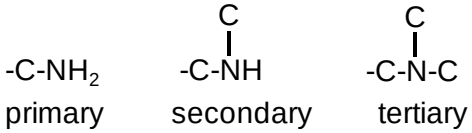

Figure 2. Amine structures pore.

Another potentially effective way to reduce the amine vapor pressure and retain it in a liquid form is to incorporate the amine functional group into an ionic liquid. Recent work has shown that ionic liquids containing all three types of amines can be synthesized and then used in SLMs that have good CO_2 permeance and improved CO_2/O_2 selectivities relative to polymeric membranes. [3] That work demonstrated that two different ionic liquid sorbents, one containing a primary amine and one containing a tertiary amine produced SLMs with promising CO_2 permeances and CO_2/O_2 selectivites. In this paper, we present additional results that show greatly improved performance with the ionic liquid containing a primary amine functional group.

II. Experimental Methods

A. Compounds Prepared

The sorbents used in this work consist of ionic liquids functionalized with an amine group. Ionic liquids are relatively low molecular weight hydrocarbon-based compounds that can have low viscosity and have effectively zero vapor pressure. Thus, they are excellent choices for use in a SLM where one side will be exposed to space vacuum. In this work, we discuss results obtained with two compounds, one containing a tertiary amine functional group, 1-butyl-4-(N,N-dimethylamino) pyridinium or B-DMAPyr, and one containing a primary amine function group, 1-(3-aminopropyl)-3-methylimidazolium or AP-Mim (Figure 3). The methods used to synthesize these compounds were described previously.[3]

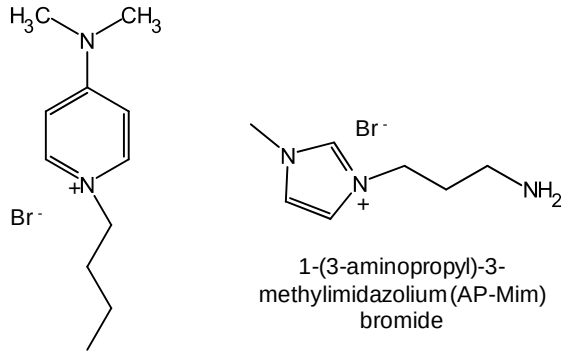

Figure 3. Structures of B-DMAP and AP-Mim functionalized ionic liquid sorbents.

B. Sorbent Characterization by and Nuclear Magnetic Resonance

Once the sorbents were prepared, they were characterized by NMR spectroscopy. To carry out this work, a JEOL NMR Model ECA-500, 500 MHz was used for NMR characterization, with D_2O or $CDCl_3$ as the solvents.

C. Gravimetric Measurement of Carbon Dioxide Uptake

Each sorbent prepared was tested to determine its CO_2 uptake capacity. A simple gravimetric set-up was selected where uptake was measured directly by weight change (Figure 4). The system consists of a manifold that delivers CO_2 or N_2 at a controlled rate into a small vial containing the candidate sorbent material. To prevent errors in weight changes, a ⅛-in stainless steel line was connected to ⅛-in nylon tube, which was immersed in the solution. When a weight was needed, the ⅛-in line was detached from the nylon tube, and the nylon tube was left in the vial.

To carry out a test, either N_2 or CO_2 was flowed through a known quantity of absorbing solution. The N_2 flow effectively reduced the partial pressure of CO_2 to zero and, from a regeneration standpoint, is identical to evacuating the systems to remove any absorbed CO_2. We carried out two types of uptake tests. We carried out total CO_2 capacity measurements where the sorbents were exposed to CO_2 or N_2 for sufficiently long periods that stable weights were achieved and no change in weight occurred with longer exposure times. We also carried out short cycle tests where the sorbents were exposed to CO_2 and N_2 for 5-minute periods to more closely simulate a membrane application. Both types of tests were conducted at sorbent temperatures ranging from 30 to 90°C.

D. Membrane Permeation Rate Measurements

A. Membrane Impregnation

The SLMs were prepared by impregnating a layered membrane consisting of two layers of Advantec PTFE membrane with ionic liquid sorbent. Each layer was 35 mm thick and had an effective pore size of 0.1 μm. As manufactured, the material is hydrophobic, however the layer on the high pressure side was treated by the manufacturer to make it hydrophilic, and easily wetted by the ionic liquid sorbent. If used as a single membrane, the pore size of PTFE would be too large to contain the ionic liquid and the pressure differential of 0.3 atm would force the ionic liquid out of the porous structure. To prevent this, an untreated, hydrophobic, PTFE membrane is placed on the low pressure side of the impregnated membrane, which effectively seals the ionic liquid sorbent inside the hydrophilic layer. The impregnation was done by placing the layered membrane in a flat dish containing the ionic liquid sorbent. The dish was placed in a vacuum oven where it was cycled between vacuum (50 mtorr) and atmospheric pressure four times to remove air from the pores and then held under vacuum at 50°C for 48 hours. Excess ionic liquid was removed from the membrane and it was then placed on top of a stainless steel mesh which rested on the bottom (low pressure side) of the membrane housing.

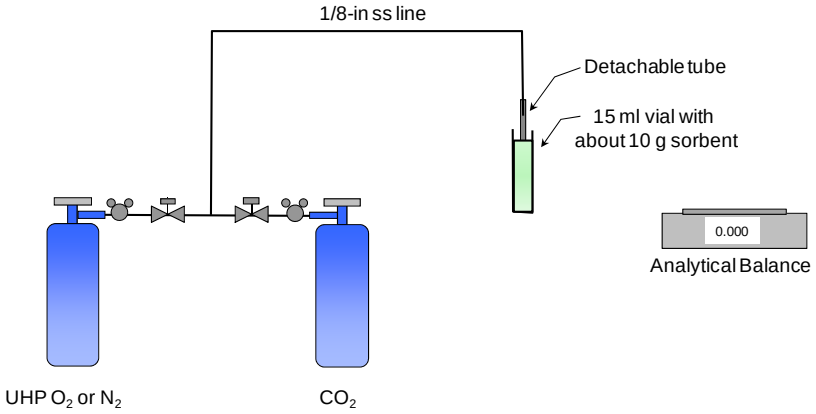

Figure 4. Schematic of the gravimetric CO_2 uptake system.

The membrane housing, which described in detail previously[3] consists of two aluminum flanges with flow passages and O-ring seals machined into each. The impregnated membrane was placed between the flanges, which were secured together with three bolts. In all tests, the flange on the low pressure side was connected to a vacuum pump to simulate the vacuum of space. Two different top flange configurations were used. In single gas tests, one port on the top flange was opened to either pure CO_2 or O_2 and the permeance of each was measured by monitoring the rate at which the pressure decreased on that side of the membrane. In mixed gas tests, we used a two port top flange that circulated the process flow into the housing, over the membrane surface, and then out of the cell housing.

B. Single Gas Test Rig

Single gas permeation measurements were made with a fixed volume test rig, which was described in detail previously.[3] Briefly, the system consists of the membrane housing, a mechanical pump capable of reaching pressures down to 20 mtorr, and a manifold that is used to expose the membrane to CO_2 or O_2 and monitor the gas flow through the membrane. The rig manifold contains a 1-liter reservoir on the high pressure side of the membrane, a 175-cc reservoir on the low pressure side and pressure transducers on both the high and low pressure sides of the membrane. To carry out a test, both reservoirs were first evacuated and then the 1-L reservoir was filled to the desired pressure with either CO_2 or O_2. To start the test, the valve that connected the 1-liter reservoir to the high pressure side of the SLM was opened, exposing the membrane to the contents in the reservoir. The permeance was then determined by monitoring the rate of pressure decrease in the high pressure side of the membrane and also the pressure rise in the low pressure side. Due to the limits on the pressure transducers the minimum exposure pressure that could be reached in this rig was 0.025 atm or 19 mm Hg.

C. Mixed Gas Test Rig

Gas permeation tests were also conducted in a mixed gas test rig. With this rig, CO_2 permeation measurements could be made under more realistic conditions, in the presence of O_2 and H_2O, and exposure pressures down to 1 mm Hg were possible. A schematic of the membrane test rig is shown in Figure 5. The system includes the flow-through test cell that holds the SLM, an oil-less scroll pump to evacuate the loop, a gas manifold to charge the loop with representative pressures of O_2 and CO_2, a diaphragm pump to circulate the mixture, analytical instrumentation to measure the changes in CO_2 and H_2O concentrations, and an 8 liter reservoir. The mixture was circulated at a rate of

about 17 slpm resulting in a circulation time of about 30 seconds. An in-line, vacuum rated rotameter and valve controlled the flow in the loop. Water was introduced in two different ways. Initially a batch addition was made with an evaporator, which quickly charged the loop with humidity and then was isolated from the flow. We then modified the system and installed a a Chemyx Fusion 100 syringe pump so that water could be added on a continual basis at a representative rate. A Vaisala relative humidity sensor was used to monitor the relative humidity (RH) in the mixed gas and the CO_2 concentration in the gas mixture was monitored with a gas chromatograph (GC). Finally, the system used LabVIEW software and National Instruments hardware for control and data acquisition.

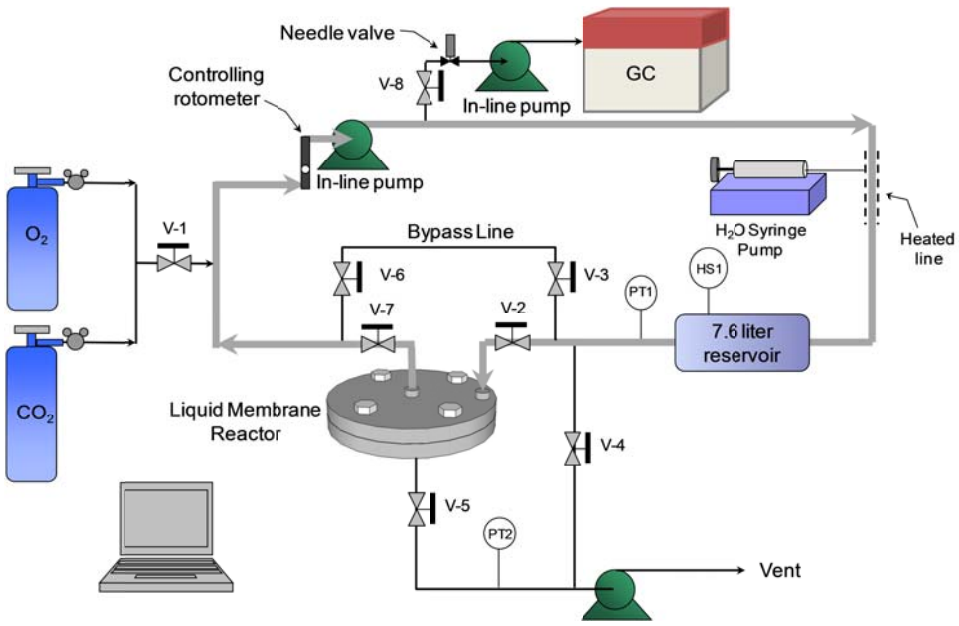

Figure 5. Schematic of the mixed gas test rig for SLM permeation testing.

To conduct gas permeation tests, the system was first evacuated to less than 50 mtorr and then the membrane was isolated by directing flow through the membrane bypass line. The loop and reservoir were then charged to 0.4 atm with a mixture consisting of low concentrations of CO_2 in O_2. In these tests the initial CO_2 concentration ranged from 0.75% to 2.5% which correspond to to CO_2 partial pressure from 1.9 mm Hg up to 7.6mm Hg. The circulation pump was started and at the same time the syringe pump was activated and water was injected at a rate of 8.0 µL/h to bring the humidity level up to the desired set point. Baseline GC measurements were obtained to verify that the expected CO_2 concentration was achieved in the loop. When the RH reached the desired starting point of about 25%, a second set of GC analyses were obtained and then the process flow was switched from the membrane by-pass loop to the flow-through cell exposing the process flow to the SLM. Measurements of CO_2 concentration in the loop were made through the course of the experiment and used to calculate CO_2 permeance; the test was stopped when the CO_2 concentration had dropped to approximately half the original starting concentration. The O_2 permeance was calculated by monitoring total pressure and correcting for the loss of humidity and losses from the GC sampling.

III. Results

A. Spectroscopic Characterization of Ionic Liquids

The NMR results obtained for the primary amine-containing compound AP-Mim are shown in Figure 6. The figure shows the predicted (top) and actual (bottom) spectra for AP-Mim. In this case, there is a good match between the predicted spectra and those observed. Of particular importance are the peaks corresponding to the protons labeled E, F, and G since these are part of the butyl group that was attached to the imidazolium ring during the synthesis. The figure shows a good match between the peaks predicted by the ChemBiodraw software and those obtained in the NMR analysis. Overall, the NMR results obtained provide good evidence that the desired compounds were synthesized.

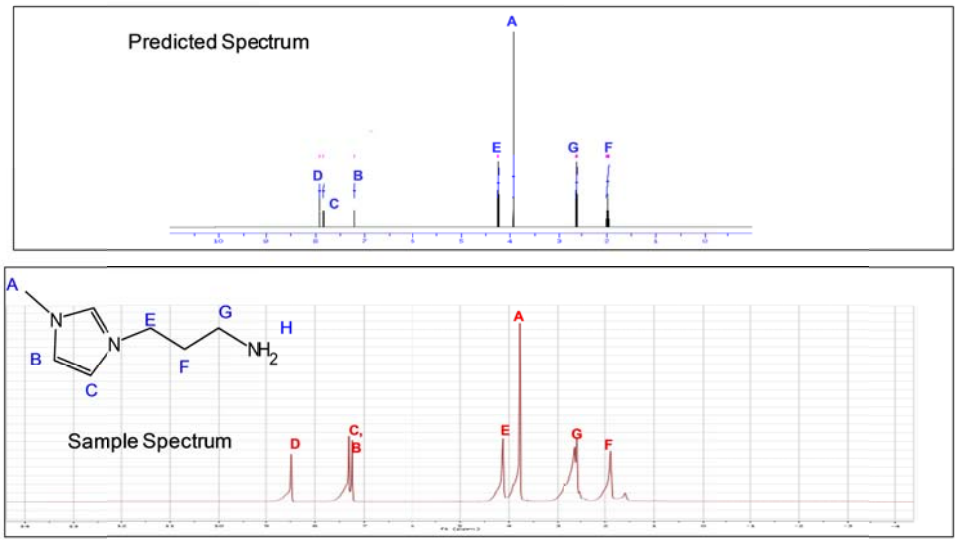

Figure 6. Predicted and measured NMR spectra of the AP-Mim.

B. CO_2 Uptake Results

The CO_2 uptake results obtained for the secondary amine (B-BAPim TF_2N) and the primary amine (AP-Mim) at temperatures from 30°C to 90°C are show in Figure 7. The figure shows that the uptakes of these two compounds have some substantial differences. First, the total uptake for the primary amine was much greater than the five-minute uptakes. For example at 50°C, the total uptake was 3.93 wt% compared to a reversible value of 0.51wt%. On the other hand for the secondary amine, the five minute reversible uptakes are identical to the total uptakes at all temperatures tested. Another difference is that for the primary amine, the reversible uptake increased to 0.94 wt% as the temperature was increased from 50°C to 70°C. However for the secondary amine, both the total and the reversible uptakes decreased as the temperature was increased. Likewise the total uptake of the primary amine decreased as the temperature was increased.

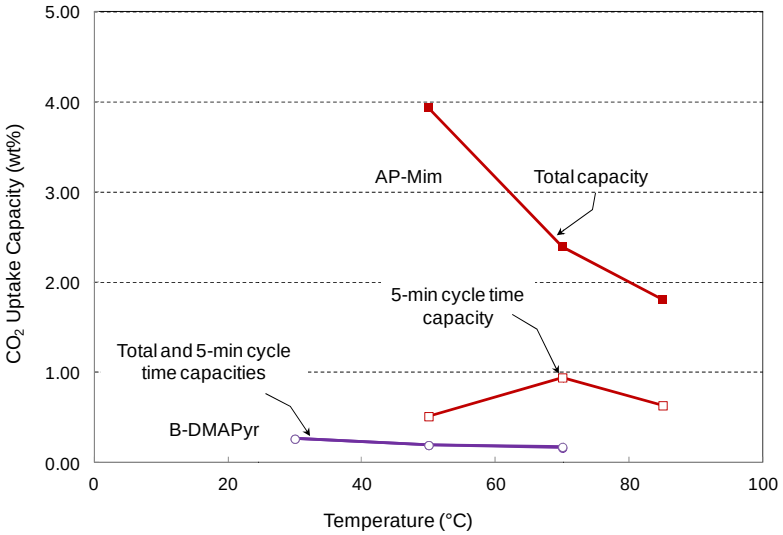

Figure 7. Summary of the total and 5 minute CO_2 uptake results for the AP-Mim and B-DMAPyr sorbents.

C. Single Gas Test Results at 0.2 atm CO_2 Pressure

Figure 8 shows the effect of using the thin, layered membrane in the SLM with the AP-Mim sorbent. The figure includes CO_2 permeation data obtained on the thin, layered membrane along with data obtained on the thicker, regenerated cellulose (RC) membrane. The latter membrane was 230 µm thick and has a molecular weight cutoff of 10,000 Daltons (10 kDa), corresponding to an effective pore size of 0.005 µm. In both cases, tests were carried out

at membrane temperatures from 30°C to 120°C and at CO_2 exposure pressures of 0.2 atm. As shown, switching to the thinner membrane resulted in significant increases in CO_2 permeance. For example at 70°C, the permeance in the RC membrane was 5.08E-7 scc/(cm^2-s-cm Hg). However, in the thinner, layered membrane the permeance increased to 7.22E-6 scc/(cm^2-s-cm Hg), which is over a factor of 10 increase. At the highest temperature of 120°C, the CO_2 permeance was 1.4E-5 scc/(cm^2-s-cm Hg), which is high enough to meet the permeance requirement. However, the figure also shows that at 70°C, the O_2 permeance was 9.3E-7 scc/(cm^2-s-cm Hg); therefore the CO_2/O_2 selectivity at this temperature was less than 10, which does not meet the selectivity requirement.

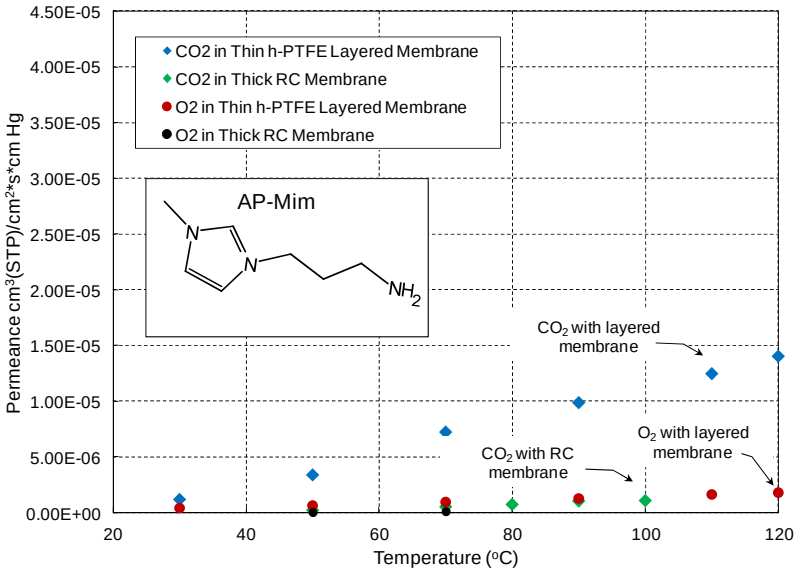

Figure 8. Permeance values obtained for the AP-Mim sorbent in the RC and thinner, layered membrane.

Although these tests produced accurate measures of CO_2 permeance through the membrane, the CO_2 exposure pressures used, 0.2 atm, were much higher than would be permitted in a space suit. Therefore in order to conduct tests under more realistic conditions, we reduced the exposure pressure by a factor of 10 and conducted tests at pressure of 0.025 atm or 19 mm Hg. The results of these tests are shown in Figure 9. The results obtained at the higher exposure pressures are included in the figure for comparison. Reducing the CO_2 exposure pressure resulted in significant increases in CO_2 permeance and because the O_2 partial pressure is not being changed, the effect translates directly into significant increases in CO_2/O_2 selectivity. For example at 90°C, reducing the CO_2 pressure from 0.2 atm to 0.025 atm increased the CO_2 permeance from 9.8E-6 to 2.0E-5 scc/(cm^2-s-cm Hg), or by about a factor of 20. At 110°C the CO_2 permeance increased from 1.3E-6 to 3.7E-5 or by a factor of 28. Moreover, at this condition the CO_2/O_2 selectivity is 25, which represents a significant increase over the selectivities that were obtained at the higher CO_2 exposure pressure of 0.2 atm.

The increase in CO_2 permeance that we observed when the CO_2 exposure pressure was decreased from 0.2 atm to 0.025 atm is referred to as facilitated transport and it has been reported previously.[11] Although 0.025 atm (19 mm Hg) is significantly lower than the pressures used previously, it still is higher than would be permitted in a space suit. Therefore there was a need to characterize the performance of the SLM under more representative CO_2 pressures, less than 2 mm Hg. In addition, the CO_2 permeance in a

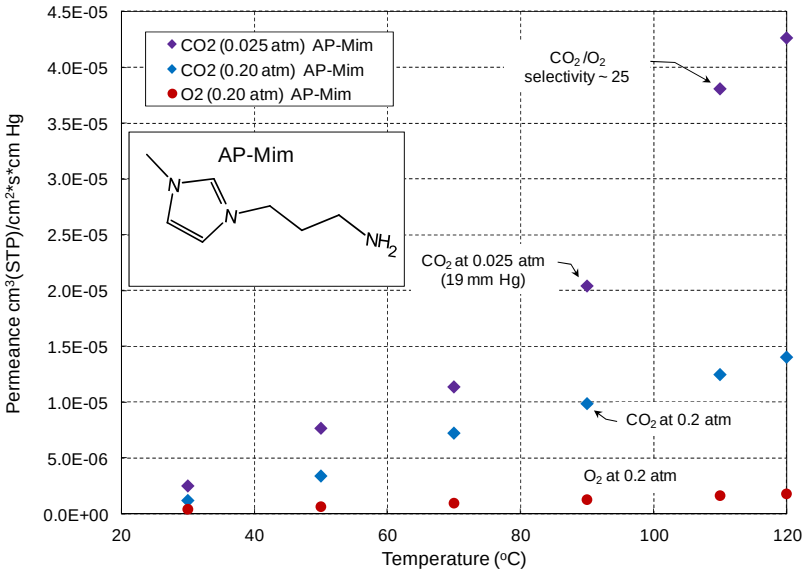

Figure 9. Permeance values obtained for the AP-Mim sorbent in the layered membrane at temperatures from 30 to 120°C.

mixed gas including water needed to determined. Therefore, we switched to the mixed gas test rig for additional tests.

Humidity addition was done in several steps. Initial tests were carried out in the mixed gas test rig without adding water. Then tests were conducted where the RH addition was done in a batch mode prior to exposing the flow to the membrane. Finally, water was added on a continual basis at a representative rate with a syringe pump. Results of each type of test are included below.

D. Mixed Gas Test Results without Humidity Addition

The results of four mixed gas tests, two with AP-Mim and two with B-BAPim are shown in Figure 10. The figure shows the CO_2 concentration measured in the flow loop with the GC as a function of membrane exposure time. In all cases the CO_2 concentrations decreased at a relatively constant rate, so that all points in each test fall close to a straight line. For the tests with the AP-Mim, the starting concentrations were approximately 1.18 mole% which corresponds to a CO_2 partial pressure of approximately 3.5 mm Hg. The figure shows that the rate of decrease in CO_2 concentration measured for the AP-Mim at 55°C was greater than that obtained at 45°C. We used the slopes of the lines to calculate average permeance values for each test and obtained a value of 6.75E-5 scc/(cm^2 s cm Hg) for the tests at 55°C and 4.32E-5 scc/(cm^2 s cm Hg) for the test carried out at 45°C.

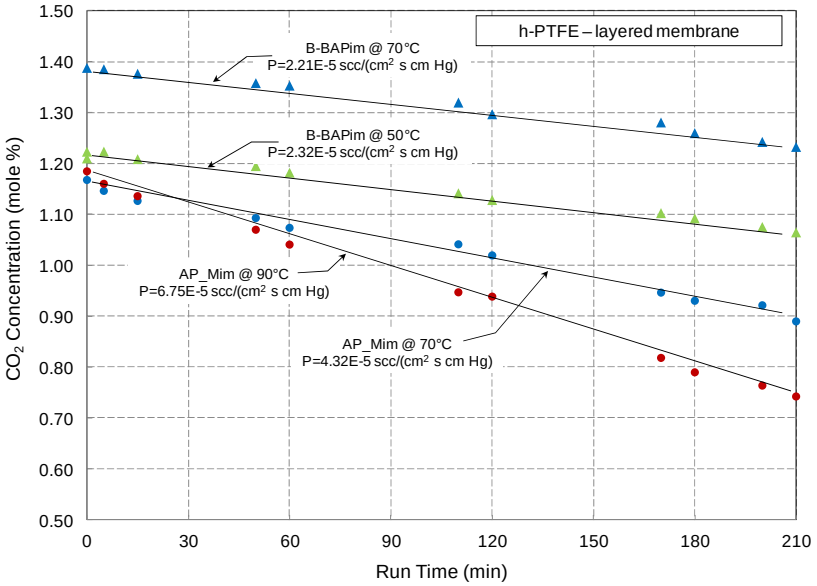

Figure 10. Measured CO_2 concentrations in the circulating loop with two different ionic liquid solutions at membrane temperatures ranging from 50 to 90°C.

Comparing these permeance values to those reported in the previous figure shows that higher values were obtained at the lower CO_2 pressures. For example, the maximum value obtained in these tests, 6.75E-5 scc/(cm^2 s cm Hg) is almost 50% higher than the maximum value reported in Figure 9. Obtaining higher permeance values at reduced CO_2 pressures is a characteristic of facilitated transport where there is a chemical reaction between the sorbent and CO_2. This characteristic has been discussed previously and is the result of the increased efficiency of the reaction between the sorbent and CO_2 as the concentration of CO_2 is reduced.[11]

The results obtained for the secondary amine, B-BAPim TF_2N at 35°C and 45°C are also contained in this figure. Initial inspection shows two significant differences from the data obtained with the AP-Mim. First in both cases, the slopes are noticeably lower than both of those obtained for the primary amine. The permeance values obtained for this compound at 35°C and 45°C were 2.32E-5 scc/(cm^2 s cm Hg) and 2.21E-5 scc/(cm^2 s cm Hg) respectively and these values are about a factor of two lower than the values obtained with the primary amine. In addition, the results with the secondary amine showed that increasing the temperature decreased the permeance value by a small amount. On the other hand, we saw that increasing the temperature by 10°C with the primary amine resulted in about a 50% increase in permeance.

We also carried out additional tests with starting CO_2 concentrations of 2.5 and 0.5 mole% which correspond to partial pressures of approximately 8 and 2 mm Hg respectively. The permeance values obtained in these tests are shown in Figure 11. The figure includes best fit lines of permeance as a function of concentration at both temperatures along with the permeance needed to support the average production rate of an astronaut while maintaining a maximum concentration of 3 mm Hg. The figure shows that at both temperatures, the permeance values increased as the initial concentration was reduced. At 45°C, we obtained a permeance of 3.14E-5 scc/(cm^2 s cm Hg) at a CO_2 partial pressure of 8.9 mm Hg, while at a lower pressure of 1.6 mm we obtained a permeance of 6.69E-5 scc/(cm^2 s cm Hg). This represents over a factor of two increase in permeance obtained by going to the lower CO_2 exposure pressure. At 55°C, the difference was even greater. At 8.83 mm Hg, we obtained a permeance of 3.89E-5 scc/(cm^2 s cm Hg), while at 1.9 mm Hg, the permeance increased to 1.04E-4 scc/(cm^2 s cm Hg).

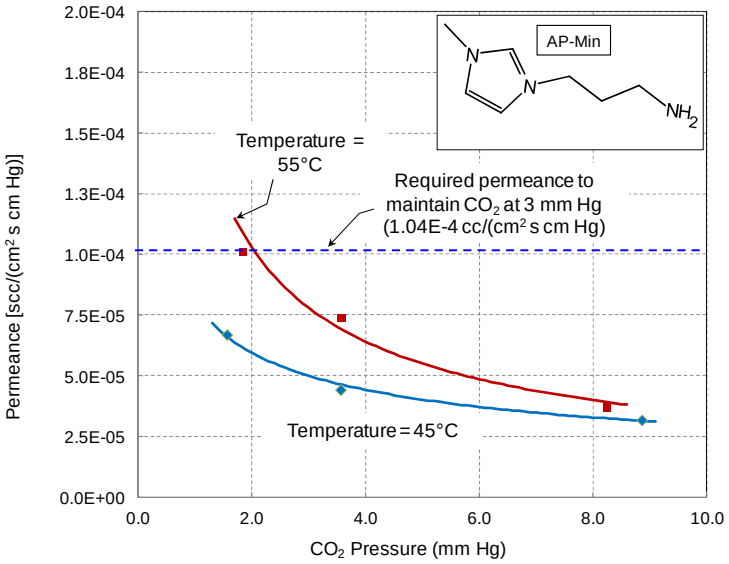

Figure 11. Permeance values obtained with the AP-Mim at 45°C and 55°C as a function of CO_2 pressure.

Figure 11 includes an estimate of the permeance that would be needed to control CO_2 in a suit assuming an average CO_2 generation rate of 93 g/h and that the module volume limit is 0.25 ft^3. With a hollow fiber configuration, the module could contain a surface area of 50m^2 which then sets the flux at 3.12E-5 scc/(cm^2 s) and if the CO_2 concentration is limited to 3 mm Hg, then the required permeance is 1.04E-4 scc/(cm^2 s cm Hg). Therefore the shows that at 90°C, the flux needs to be increased by about 25% to reach the required permeance at a CO_2 concentration of 3 mm Hg.

The flux through the membrane is the product of the permeance and the CO_2 partial pressure and therefore we can use the permeance models to calculate the expected CO_2 flux through the membrane as a function of CO_2 partial pressure at 45°C and 55°C with the AP-Mim. The results of these calculations are shown in Figure 12. The figure shows that even though the permeance increased with reduced partial pressure, the flux through the membrane increased as CO_2 partial pressure increased. At 55°C, the calculated flux increased from 2.2E-5 scc/(cm^2 s) at a CO_2 pressure of 2 mm Hg up to 3.4 E-5 scc/(cm^2 s) at a CO_2 pressure of 10 mm Hg. At 45°C the values were somewhat lower as expected from the lower permeance values reported in the previous figure. At this

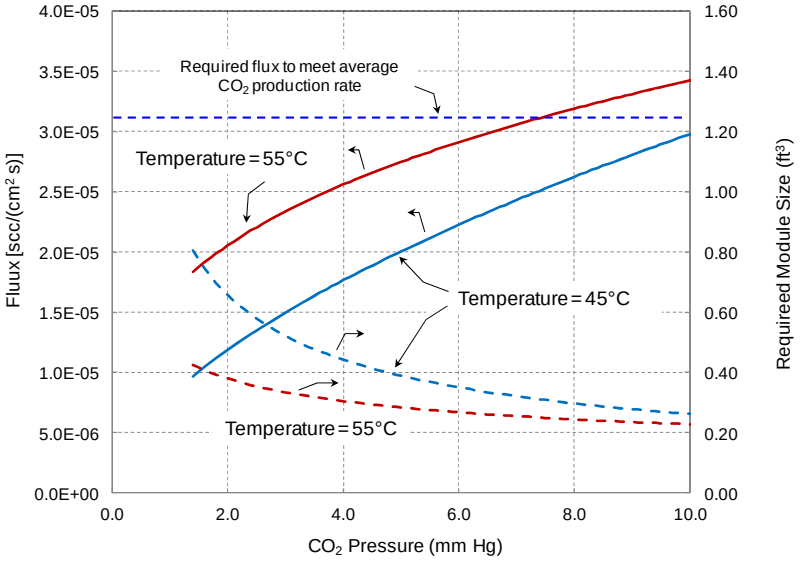

Figure 12. Calculated CO_2 flux through an AP-Mim membrane and module size that would be required as a function of CO_2 pressure.

temperature, the maximum value was 3.0E-5 scc/(cm^2 s) at an exposure pressure of 10 mm Hg. The figure also includes the average flux that is needed to meet the average CO_2 production rate and that value is 3.1E-5 scc/(cm^2 s). At 55°C, the membrane reached this flux at a concentration of about 7.5 mm Hg. Since recent work suggests that maintaining the CO_2 level at or below 3 mm Hg will be beneficial to crew health, the figure shows that although the permeance values are close to meeting the needed flux, more improvement is still needed.

We also used the flux values to calculate the required module volume to support the CO_2 production rate and those values are shown in the dashed lines in **Figure 12**. The figure shows that at a partial pressure of 3 mm Hg a module would occupy a volume of approximately 0.33 ft^3 which is somewhat larger than the current target volume of 0.25 ft^3.

E. Mixed Gas Test Results with Batch Water Addition

Although conducting tests in a dry environment provides valuable information, the membrane must function in the presence of moisture which is generated by a crew member. Current estimates show that average moisture generation rates are approximately 80 g/h which is about two times the molar generation rate of CO_2. In addition to the moisture generated by crew from exhaled breath, it is also produced from sweat.

Two types of tests were carried out in the presence of water. In the initial set of tests, we used a saturator (not shown in Figure 5). In these tests, the circulation loop was opened to a saturator for a short time, which brought the humidity level up in the loop quickly and then the saturator was closed off from the system. Therefore in these tests, we calculated the permeation rate using the slope of the RH and used an intermediate RH level as the initial exposure pressure.

To carry out the test with moisture, we first charged the loop with O_2 to 0.4 atm and then added CO_2 to the desired concentration. We then isolated the membrane and exposed the loop to the water-containing reservoir. During this time, we monitored the relative humidity with the sensor and found that the humidity increased rapidly and reached a value of approximately 50%. We then isolated the water reservoir by directing the gas flow through the by-pass and after steady state conditions were established, opened the loop to the membrane.

The results of this test are shown in Figure 13. The figure shows that before the loop flow is open to the membrane, the RH was stable at approximately 52% and the CO_2 values were also relatively constant at 0.98 mole %, which corresponds to approximately 4 mm Hg. At a run time of 58 minutes, when the loop was open to the membrane, the figure shows that the CO_2 concentration dropped at a relatively constant rate and reached a value of 0.71 mole % at the end of the test period. Using the slope of the line and the initial exposure pressure, we determined that the CO_2 permeance was 5.05E-5 scc/(cm^2 s cm Hg). Figure 13 also shows that when the membrane was open to the flow loop, the humidity dropped rapidly reaching a value of about 10% at a time of 92 minutes or after only 30 minutes exposure to the membrane. As shown the RH continued to drop and at the end of the test had reached a value of less than 1%. We used the data to calculate an average H_2O permeance and obtained a value of 1.3E-3 scc/(cm^2 s cm Hg). This

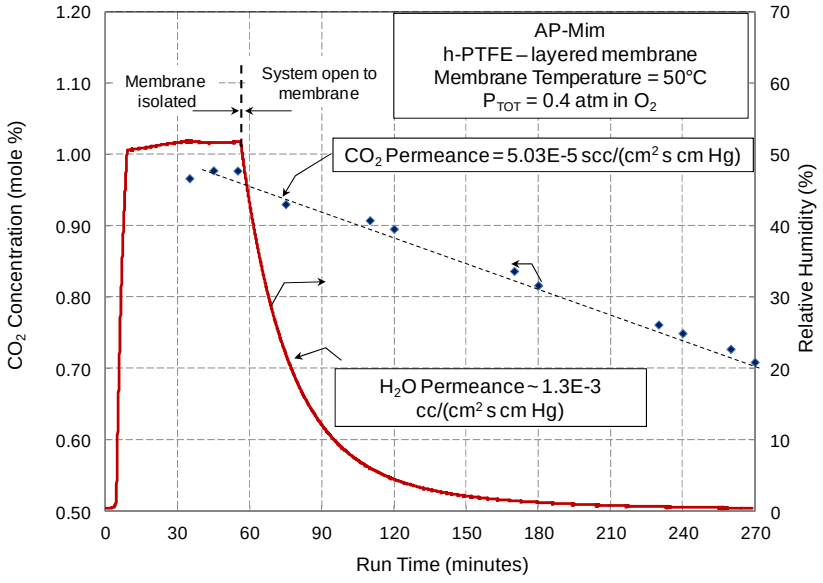

Figure 13. CO_2 and relative humidity as a function of run time exposed to an SLM with the AP-Mim.

value is a about a factor of 50 greater than the CO_2 permeance and indicates that the membrane could control the humidity levels in a space suit to very low values.

During the test we monitored the pressure on the low pressure side of the membrane, which was continually being pumped during the test by the scroll pump. In Figure 14, we present this data along with the relative humidity shown in the previous figure. This figure shows that at the time when the loop flow was opened to the membrane and the relative humidity dropped rapidly, a small pressure increase occurred in the lines downstream of the membrane. This indicates that the moisture that was being removed from the loop was passing through the SLM and was not simply dissolving in the liquid. This behavior is critical to the operation of the membrane since if moisture simply dissolved in the liquid, it would eventually reach capacity and stop being effective.

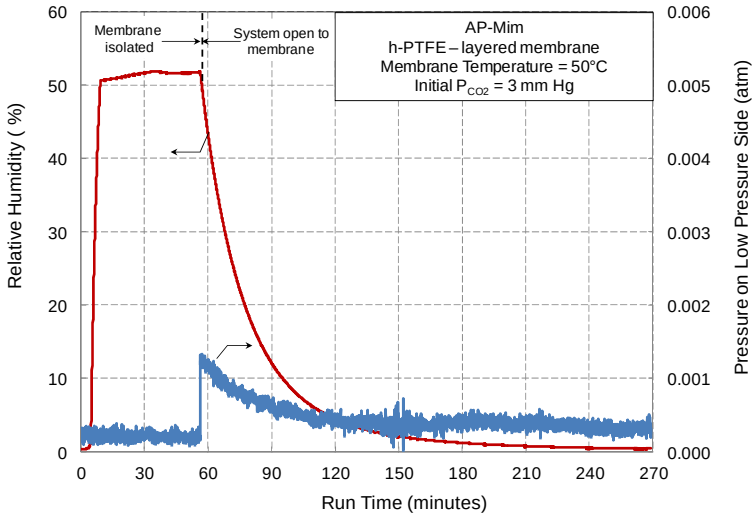

Figure 14. Humidity level in the circulating loop along with the pressure in the lines on the low pressure side of the membrane.

F. Mixed Gas Test Results with Constant Water Addition Rate

Although the results in the mixed gas tests with the AP-Mim showed that the permeance values were approaching those needed to control CO_2, the O_2 permeance values were still too high resulting in a CO_2/O_2 selectivity of 89. Although this is a much higher value than can be obtained by conventional membranes, it is well below the 1300 threshold that we identified earlier. Therefore we switched to a different anion which has been suggested to be more resistant to O_2 permeation. In addition, we switched our water addition to a continual mode using a syringe pump.

The results of our initial test with this compound are shown in Figure 15 and Figure 16. Figure 15 shows the CO_2 concentration, plotted on the left axis, and the relative humidity profile, on the right axis, as a function of time, both before and after the circulating loop was exposed to the

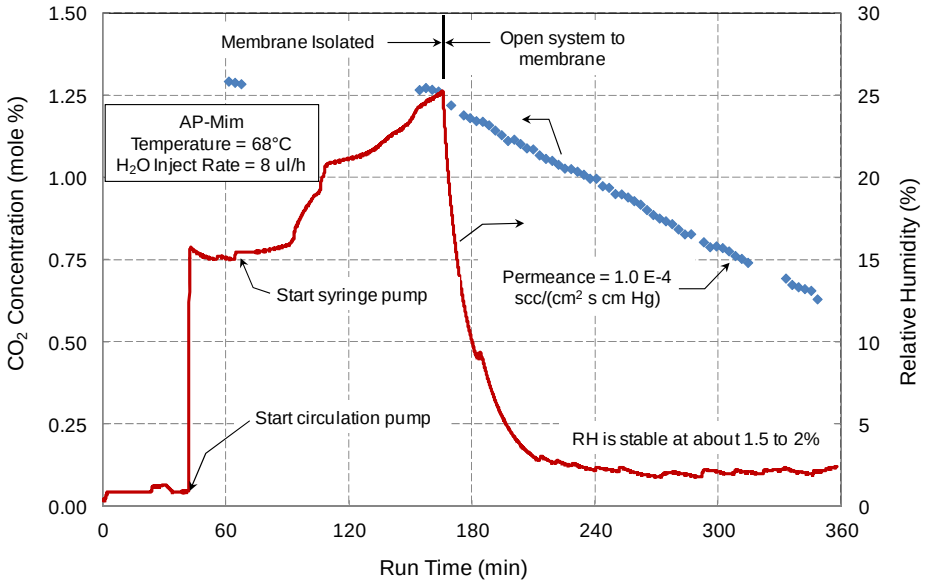

Figure 15. CO_2 concentration and moisture as a function of time with the AP-Mim at 68°C.

membrane. Between time zero and 41 minutes, we charged the large reservoir and loop with CO_2 and O_2, using the procedure described above, such that the membrane containing the ionic liquid sorbent was not yet exposed to the gas. At a time of 41 minutes, the circulation pump was activated which brought the relative humidity level up to 15%. After maintaining these conditions for 15 minutes, we activated the syringe pump and also obtained a CO_2 measurement with the gas chromatograph. As shown we obtained three similar values that averaged 1.29 mole %. Figure 16 shows that the total pressure of the system is 0.41 atm and therefore a concentration of 1.29% is equivalent to a partial pressure of 4 mm Hg. At 65 minutes we activated the syringe pump which caused the relative humidity to climb to 25% as expected and at 160 minutes we obtained another set of GC analyses that show the CO_2 concentration was remaining relatively constant. Finally at 165 minutes, we closed off the membrane bypass and directed the gas flow through the high pressure side of supported liquid membrane test cell. The figure shows that after exposure to the membrane, the relative humidity decreased rapidly and reached a value of 5% at 96 minutes and eventually stabilized at approximately 2.5 to 3% for the duration of the test. The figure shows that the CO_2 concentration also dropped rapidly after the flow was exposed to the membrane. Over this range the decrease in CO_2 concentration was relatively linear and reached a value of 0.63% at a time of 349 minutes. We used the slope of the CO_2 concentration vs time to calculate a permeance of 1.0 E-4 scc/(cm^2 s cm Hg).

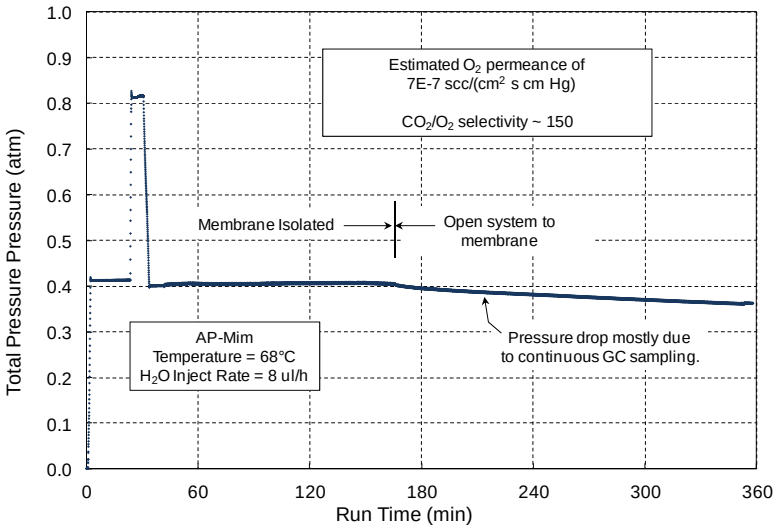

Figure 16. Total pressure as a function of time with the AP-Mim at 68°C.

Figure 16 shows the total pressure as a function of time. The figure shows that before the loop was exposed to the membrane, the system was charged with our calibration gas (2.5 mol % CO_2, balance O_2) to a pressure of 0.4 atm. Pure O_2 was then added to bring the system pressure up to just over 0.8 atm (atmospheric pressure at our facility in Golden CO), thereby reducing the CO_2 concentration to approximately 1.25 mol%. The system pressure was then reduced to 0.4 atm. This sequence was used to drop the CO_2 concentration to the desired value of 3.8 mm Hg. The pressure remained constant until the loop was opened to the membrane and then the figure shows that the pressure dropped at a relatively constant rate and reached a value of 0.37 atm at the end of the test. The pressure decrease shown here was the result of three factors: constant removal of gas for GC sampling, loss of water vapor through the membrane, and CO_2 and O_2 permeance through the membrane.

As mentioned in the test procedures, we corrected for the losses due to CO_2, GC sampling, and water vapor loss and arrived at a O_2 permeance of 7E-7 scc/(cm^2 s cm Hg). Compared to the CO_2 permeance, we obtained a CO_2/O_2 selectivity of 150, a significant increase from the values we obtained with the AP-Mim with the original anion.

Although the previous results we obtained were very positive, the O_2 permeance was low enough that the change in pressure from GC sampling was causing significant uncertainty in the calculation of O_2 permeance. Therefore, to achieve better accuracy in our O_2 permeance calculations, we modified the testing procedure slightly in subsequent runs. Rather than operating the GC sampling pump continually, we conducted a test in which we only operated the pump for three short periods during the test: right before the syringe pump is started to obtain initial CO_2 after charging the reservoir with CO_2, just before the loop is open to the membrane and finally once at the end of the test after the membrane is isolated from the circulating flow. The data in Figure 15 show that the change in CO_2 concentration is linear so using values at the start and end of the test will result in the same value as continual GC

measurements. Moreover, this will reduce the uncertainty in the O_2 permeance value by greatly reducing the pressure loss due to GC sampling.

The results of the test run with the revised procedure are included in Figure 17 and Figure 18. Figure 17 shows the same relative humidity behavior during the test as shown in the Figure 15. Before the loop was exposed to the membrane, the relative humidity increased and then after exposure, the RH dropped to about 1.5 to 2% as in the previous test. The initial CO_2 values in this test were 1.18%, slightly lower than those in the previous test but still in a representative range of 3.6 mm Hg. At a run time of 344 minutes, after being exposed to the membrane for 183 minutes, the CO_2 concentration dropped to 0.79% which resulted in a permeance of 7.0 E-5 scc/(cm^2 s cm Hg), which is 70% of what we observed previously. This can be explained by the slightly lower temperature of this test (66.7^{o}C vs. 68^{o}C) in a system where performance is very temperature sensitive.

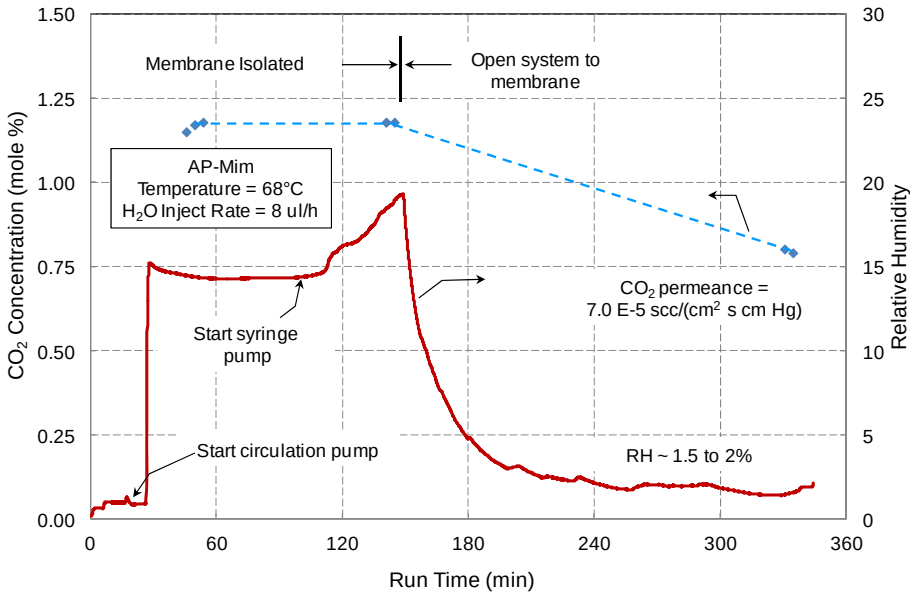

Figure 17. CO_2 concentration and moisture as a function of time with the AP-Mim at 67°C.

Figure 18 shows the total pressure obtained during the test. In this case the magnitude of the pressure drop was much lower than in the previous test, reflecting the pressure loss by the continuous operation of the GC sampling pump. In this case the pressure only dropped from 0.40 to 0.39 atm. The initial pressure drop just after the loop is opened to the membrane is due almost entirely to the rapid loss of water vapor. After that the pressure is very stable.

We used this data to calculate an O_2 permeance of 3.6E-7 scc/(cm^2 s cm Hg), which is about half the value obtained in the previous tests. Using the CO_2 and O_2 permeance values we obtained a selectivity of 190 with this form of the AP-Mim at 67°C.

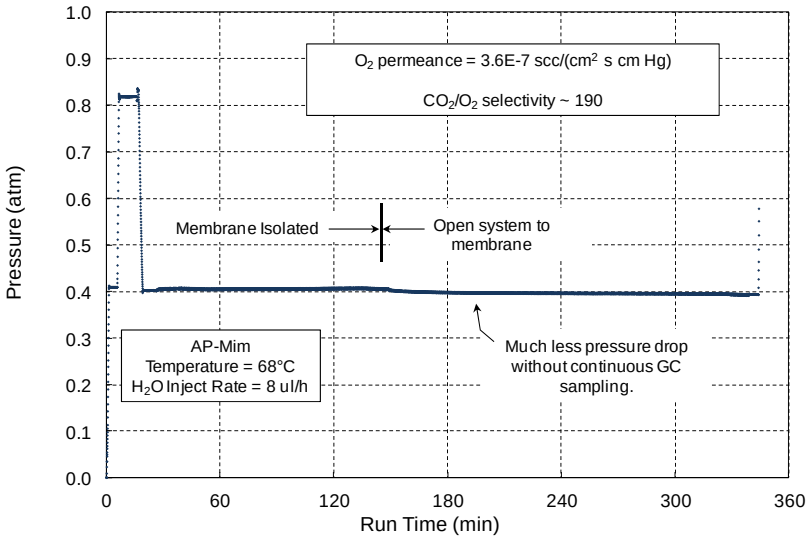

Figure 18. Total pressure as a function of time with the AP-Mim at 67°C.

We then repeated the test at a slightly higher temperature, 75°C. The results of this test are included in Figure 19 and Figure 20. Figure 19 shows that once again the moisture dropped rapidly when the circulating gas was exposed to the membrane and again reaches a steady state concentration of about 2 to 3%. In addition the figure shows that the CO_2 concentration dropped from 1.21 to 0.58% over the duration of the run, resulting in a permeance of 1.1E-4 scc/(cm^2 s cm Hg). This value is approximately twice as high as the value obtained in the previous figure and demonstrates that temperature has a strong effect on the rate of CO_2 removal in this system. Moreover, this permeance meets the performance goal established earlier and therefore a unit sized to control the average CO_2 production from a crew member could be contained in a module that is no larger than 0.25 ft^3.

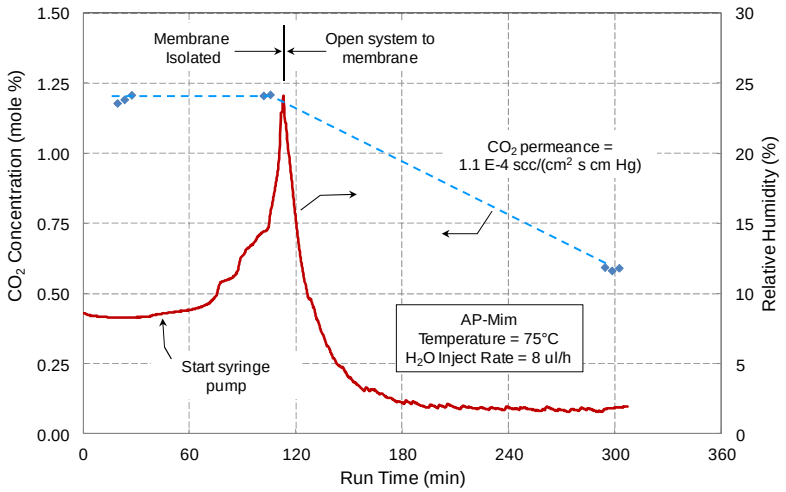

Figure 19. CO_2 concentration and moisture as a function of time with the AP-Mim at 75°C.

The total pressure measurement for this test is shown in Figure 20. In this case, there was very little pressure drop after the loop was exposed to the membrane. Once again immediately after the loop was opened to the membrane there was a noticeable pressure drop, which was due primarily to the loss of water vapor, as shown in Figure 19. However after that change, the pressure remained very constant. For example, Figure 20 shows that the pressure was 0.3949 atm at 180 minutes; however at 300 minutes or two hours later the pressure had only dropped to 0.3929 atm. This difference is very small and is right at the resolution of our pressure transducer. Therefore, we estimated that the permeance obtained during this run was < 3E-7 scc/(cm^2 s cm Hg). Combining this value with the CO_2 permeance reported above, results in a CO_2/O_2 selectivity of > 350.

The results presented in Figure 19 and Figure 20 are very positive and demonstrate that we have reached the required value for permeance and are also approaching the CO_2/O_2 selectivity target. Although a selectivity of >350 is encouraging, the O_2 permeance was less than our detection limit in this test rig. Therefore, we repeated the O_2 permeance test in the single-gas test rig, which for O_2 permeance has a lower detection limit than the mixed gas test rig.

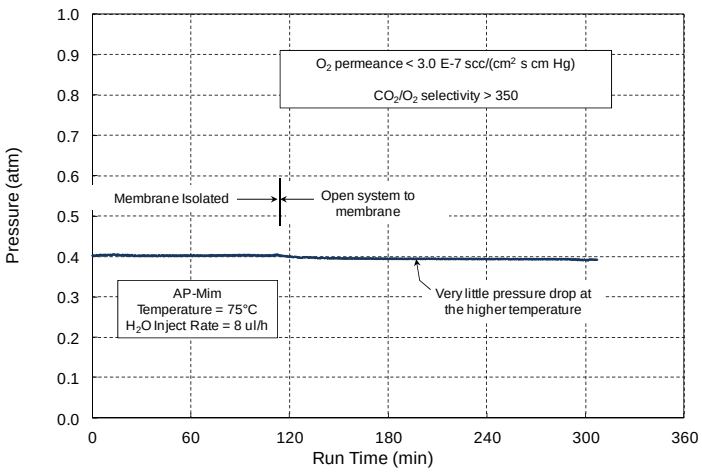

Figure 20. Total pressure as a function of time with the AP-Mim at 75°C.

The results of the static tests for O_2 with the modified AP-Mim are shown in Figure 21. The figure shows that the pressure in the upper reservoir decreased from 0.3960 atm to 0.3955 atm over a period of 50 minutes. Likewise the pressure in the lower reservoir, which has only 1/6 the volume of the large reservoir, increased from 0.002 atm to 0.004 atm over the same time period. Using the data in the figure we obtained an O_2 permeance of 7.6E-8 scc/(cm^2 s cm Hg). Using this value along with the CO_2 permeance reported in Figure 19, we calculated that CO_2/O_2 selectivity of this ionic liquid at a temperature of 75°C is 1450. This value is

greater than our initial target value of 1300 and therefore these results show that we have achieved the target CO_2 permeation and CO_2/O_2 selectivity requirements that we established. These are very positive results and demonstrate the potential feasibility of using a supported liquid membrane for CO_2 control.

In Figure 22 we have included the permeance data obtained with this form of the AP-Mim on the chart showing previous results obtained with the other anion. We also included the permeance necessary to maintain the CO_2 concentration at an average level of 3 mm Hg. As shown, the permeance value we obtained at 75°C, 1.1E-4 scc/(cm^2 s cm Hg) exceeds the requirement of 1.05 scc/(cm^2 s cm Hg). Moreover, the O_2 permeance results in a selectivity of 1450, which exceeds the target value of 1300 we established previously.

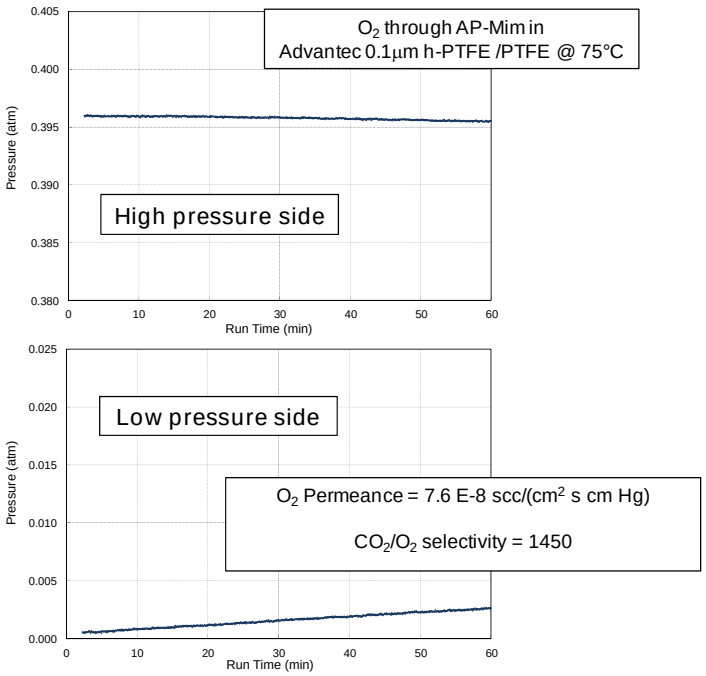

Figure 21. O_2 permeation results obtained for AP-Mim in the h-PTFE/PTFE layered membrane at 75°C.

C. Project Status

In this project we have obtained CO_2 permeance and CO_2/O_2 selectivity values that meet or exceed the benchmark performance levels and therefore demonstrate the feasibility of using a membrane for CO_2 control in an EVA. In addition, we have shown that the membrane has a very high H_2O permeance and therefore could also be used to control RH in the suit. Using a membrane to control CO_2 and RH has many advantages over competing methods and therefore these results represent the potential for a solid step forward in PLSS technology. Although the results we have obtained are very promising, they were obtained in a flat sheet configuration and the membrane must be converted to a hollow fiber form to meet size requirements. Moreover, the hollow fibers must simulate the layered form that has shown promise in the flat sheet tests and these are not commercially available. However, Reaction Systems has developed an approach to fabricating custom two-layer hollow fibers and are currently working on incorporating our sorbent into modules containing the layered hollow fibers.

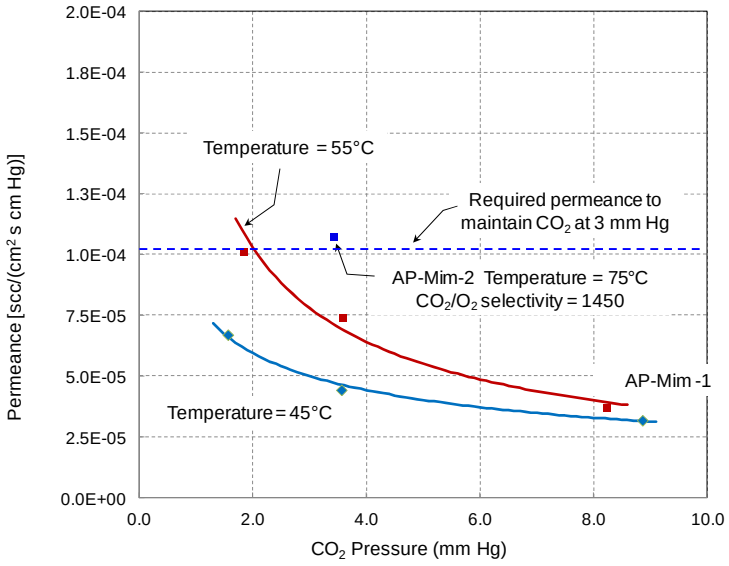

Figure 22. Permeance values obtained with the original formof the AP-Mim (AP-Mim-1) at 45°C and 55°C as a function of CO_2 pressure and the value obtained with AP-Mim-2 at 75°C.

IV. Summary and Conclusions

Overall, the results reported here show that SLMs containing custom amine-functionalized ionic liquids have the potential to separate CO_2 from O_2 in EVA applications. We have prepared new sorbents that have low viscosity, good reversible CO_2 absorption capacity, and perhaps most important, they have effectively zero vapor pressure so they can be exposed to the vacuum of space without being lost by evaporation. NMR analyses indicated that the ionic liquids prepared were consistent with the intended compounds. We demonstrated that impregnating a thin, layered membrane with our AP-Mim sorbent produced permeation rates that are high enough that if contained in a hollow fiber module would meet the volume limitation of 0.25 ft^3. Moreover, we achieved a CO_2/O_2 selectivity of 1450, and therefore the O_2 losses through the membrane would be less than the expected leak rate in suit. The results also show that the SLM has very high H_2O permeation rate and therefore the SLM can be used for moisture control.

Acknowledgments

The authors gratefully acknowledge funding for this work, which was provided by the NASA Small Business Innovative Research office under Contract NNX12CA65C.

References

[1] Barta, D.J. and Ewert, M.K. "Development of Life Support System Technologies for Human Space Exploration", SAE Paper 2009-01-2483, *39th Int. Conf. on Environmental Systems*, Savannah GA, 2009.

[2] Barta, D.J., Ewert, M.K., Anderson, M.S., and McQuillan, J. "Life Support System Technology Development Supporting Human Space Exploration", SAE Paper 2008-01-2185, *38th International Conference on Environmental Systems*, San Francisco CA. 2008.

[3] Wickham, D.T., K J. Gleason, J. R. Engel, S. W. Cowley, and C. Chullen (2013). "Advanced Supported Liquid Membranes for CO_2 Control in Extravehicular Activity Applications", AIAA Paper No. 2013-3307, 43rd International Conference on Environmental Systems, Vail CO.

[4] James, J.T. and S.M. Zalesak (2013). "Surprising effects of CO_2 exposure on decision making", AIAA Paper No. 2013-3463, 43rd International Conference on Environmental Systems, Vail CO.

[5] Papale, W. and H.L. Paul (2007). "Development Status of an EVA-sized Cycling Amine Bed System for Spacesuit Carbon Dioxide and Humidity Removal", SAE Paper 2007-01-3272, 37th International Conference on Environmental Systems, Chicago IL.

[6] Swickrath, M.J., C. Watts, M. Anderson, S. McMillin, C. Broerman, A. Colunga, and M. Vogel, (2012) "Performance Characterization and Simulation of Amine-based Vacuum Swing Sorption Units for Spacesuit Carbon Dioxide and Humidity Control," AIAA Paper No. 2012-3461, *42nd International Conference on Environmental Systems*, San Diego, CA.

[7] Papale, W, J. O'Coin, R. Wichowski, C. Chullen, and C. Campbell (2013). "Rapid Cycle Amine (RCA 2.0) System Development", AIAA Paper No. 2013-3309, 43rd International Conference on Environmental Systems, Vail CO.

[8] Dillon, P., Thomas, G., Oliver, J., and Zapata, F. "Flexible Packaging Concept for a Space Suite Portable Life Support System", SAE Paper 2009-01-2345, *39th International Conference on Environmental Systems*, Savannah, GA., 2009.

[9] Seader, J.D. and Henley, E.J. *Separation Process Principles*, John Wiley and Son, Inc. New York, 1998.

[10] Watts, C., Campbell, C., Vogel, M., and Conger, B., "Space Suit Portable Life Support System Test Bed (PLSS 1.0) Development and Testing." AIAA Paper 2012-3458, 42nd *International Conference on Environmental Systems*, San Diego CA, 2012.

[11] Hanioka S., Maruyama T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F., and Goto, M. "CO2 Separation Facilitated by Task Specific Ionic Liquids Using a Supported Liquid Membrane," Journal of Membrane Science, 314, pp. 1-4, 2008.